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Modification and Evaluation of a Thermally Desorbable Passive Sampler for Volatile Organic Compounds in Air

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The effect of fluctuating concentration on the sampling rate of a thermally reversible passive sampler is discussed, and guidelines are presented for minimizing the error associated with this phenomenon. A modified passive sampler developed using these guidelines is described, and results of laboratory tests of this device are given.

In two previous papers (*1*, *2*), we described the development and evaluation of a thermally desorbable passive sampling device, PSD, and we presented both a generalized performance model for such devices and a simplified model that is applicable to thin PSD's. In brief, the simplified model describes the time dependence of the time-weighted average sampling rate, R, as a function of the initial sampling rate, R_0, the weight of sorbent, W, and the retention volume for the sorbate/sorbent pair, V_b, viz.

$$R/R_0 = (1 - e^{-kt})/kt \quad (1)$$

where

$$k = R_0/WV_b \quad (2)$$

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We showed that the PSD, in its original configuration, was applicable for long-term (12–24 h) sampling of volatile organic compounds having retention volumes (on Tenax GC) greater than 200–300 L/g or for short-term sampling (a few hours) of chemicals having retention volumes of 50–100 L/g. However, sampling outside of these limitations was inappropriate because of the fact that the sampling rates change severely with time, a phenomenon that can lead to biased data. Furthermore, the development of these equations assumed that the exposure condition was constant. This paper addresses the problem of sampling error as a consequence of variable exposure conditions and explores the relationships between sampling error, sampling time, and retention volume. We present a modified device having reduced intrinsic sampling rates (R_0) that was developed to permit longer term sampling of chemicals having small retention volumes.

PSD SAMPLING ERROR

In our previous discussions (*2*) we showed that the sampling rates of the unmodified PSD changes with time, and we asserted that a severely changing rate (i.e., a large value of k) coupled with fluctuating exposure conditions could lead to discrepancies between the actual concentrations and those calculated using eq 1. This implies that, regardless of the physical design of the PSD, care must be taken in sampling for chemicals having very low retention volumes. It is therefore important that some guidelines be provided for considerations of specific sampling applications in order to minimize the chance for sampling error.

In a real field sampling situation, the concentration of a given contaminant can vary during the course of the sampling experiment. This variation in concentration is normally accommodated by assuming that the rate of change is slow with respect to the rate of approach to a steady-state condition at the sampling device, i.e., that a pseudo-steady-state condition exists. In such cases, we can use the differential form of eq 1 (see eq 15 of ref 2)

$$\frac{dC_s}{dt} = \frac{R_0}{WV_b}(C_\infty - C_s) \qquad (3)$$

to explore the question of how the real sampling rate varies with changing exposure conditions. Here, C_s is the vapor concentration of sorbate at the surface of the sorbent bed, and C_∞ is the external concentration. With eq 3, we can allow the external concentration to vary, while performing a numerical integration of the equation to find the real sampling rate. If the fluctuation in concentration is allowed to be severe, but remain within reasonable bounds, the actual sampling rate can be compared with eq 1 and we can develop a reasonable "worst case" estimate of the sampling error.

As an example, consider the case of 24-h sampling within a building having an average air exchange rate of 0.5 h^{-1}. Typical fluctuations of vapor concentrations in the atmosphere appear to consist of more or less random fluctuations having relatively short periods and small amplitudes superimposed on a more intense and broader base of variations having periods of several hours or more. On the basis of examination of a limited set of data, it appears that changes in this base concentration may be relatively large when viewed over times of days to weeks but are generally within a factor of 2 of the mean during a 24-h period. For the purpose of this example, let us assume

$$C_{out} = 2 + 5 \sin (0.02t) \qquad (4)$$

with clipping of the function at $C_{out} = 0$ (C_{out} is not allowed to be negative), where t is in minutes. This yields a strongly fluctuating outdoor concentration with a period of about 5 h, and an average value of 2.95 ppbv (see Figure 1). The

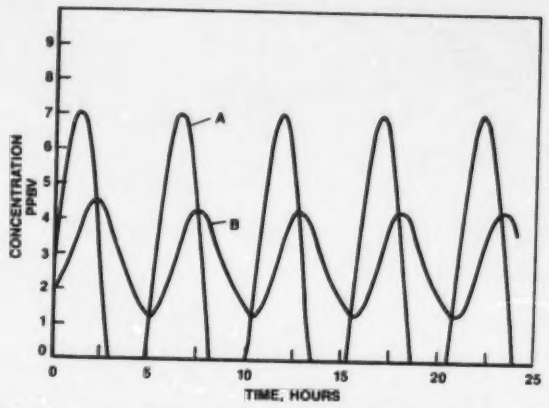

Figure 1. Outdoor (A) and indoor (B) concentration profiles for test cases.

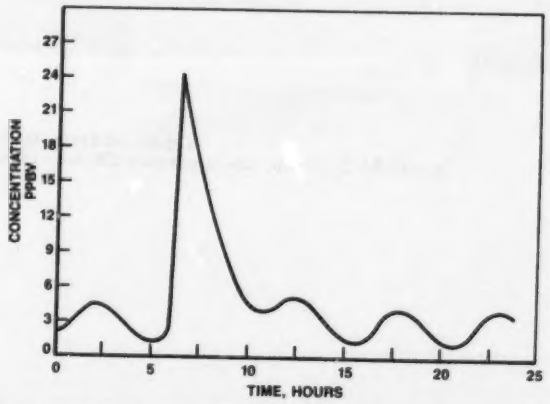

Figure 2. Indoor concentration profile with indoor source.

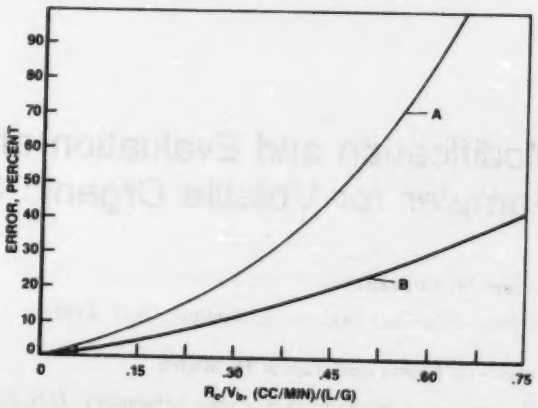

Figure 3. Sampling error due to concentration fluctuations: (A) with indoor source; (B) without source.

corresponding indoor concentration, also shown in Figure 1, can be obtained from the mass balance

$$dC_{in}/dt = F(C_{out} - C_{in}) \qquad (5)$$

where F is the air exchange rate ($time^{-1}$). It can be seen that the outdoor fluctuations are strongly buffered inside the building. A second case, where there is an indoor source that is active for 30 min and is strong enough to increase the indoor concentration by about an order of magnitude, is shown in Figure 2. The profiles for both cases, with and without the indoor source, were used in conjunction with eq 3 to determine the sampling error (relative to the numerically integrated values) as a function of the ratio of the initial sampling rate

Figure 4. Modified passive sampling device.

to the retention volume of the sorbate (see Figure 3). For these calculations, the weight of sorbent, W, was 0.44 g.

If we can regard a 10% error as a reasonable acceptable maximum, then the two curves shown in Figure 3 suggest maximum values of R_0/V_b of 0.17 and 0.32 for the respective cases with and without an indoor source. Of course, these examples are for 24-h sampling, and the critical values of R_0/V_b can be scaled appropriately for shorter sampling periods. It should be noted that the sampling error can be either positive or negative depending on the actual timing of fluctuations during the sampling period, with fluctuations occurring near the beginning of the sampling period having a more severe effect than those occurring near the end of the period. Indeed, one can devise scenarios for which the sampling error is very small even for chemicals having small retention volumes. However, inasmuch as there is usually no a priori way of knowing when fluctuations occur in real field sampling conditions, data for chemicals with R_0/V_b values exceeding the critical levels should be regarded with suspicion. Alternatively, sampling periods can be adjusted to appropriate levels to compensate for potential errors in sampling for chemicals with low retention volumes.

EXPERIMENTAL SECTION

In principle (see eq 1 and 2), the time dependence of the sampling rate can be reduced by (a) reducing the intrinsic sampling rate (R_0), (b) increasing the weight of sorbent, and/or (c) utilizing sorbents having greater retention volumes for sorbates of interest. Choice (b) is undesirable because it would require increasing the size of the PSD. Choice (c) is certainly possible, and may even be desirable for some applications, but it would require detailed information of retention volumes for other sorbents, data that is not generally available. On the other hand, the intrinsic sampling rates can be varied in a relatively predictable manner by simply altering the diffusion barriers of the PSD, and the possibility of interchangeable diffusion barriers offers an additional dimension of flexibility of applications for the PSD. Also, reduction of the intrinsic sampling rate should yield an additional benefit of reducing the sensitivity of the sampling rate to the external air velocity (see ref 1).

In the current work, several different alternative designs for replacement diffusion barriers were considered. These included (a) the use of filter paper to fill the void between the first and second screen assemblies of the PSD, (b) the use of finer screen, (c) the use of compound plate assemblies with holes in the second plate being offset from those in the first, and (d) the use of a single plate having a single small hole as a replacement for the standard outer screen assembly of the PSD. Simple calculations of the effective area to length ratios for various possibilities showed that only the latter two choices were capable of yielding the desired effect. In view of the simplicity of the single plate concept, that approach was adopted. Reduced-rate devices were prepared by replacing the outer screens and perforated plates (inner screens and plates were retained) of the standard PSD with single 0.030-in. (0.076-cm) stainless steel plates having single 0.5-mm holes at their centers. The diameter of the plates was sized to yield a tight "press fit" when inserted into the PSD, thus ensuring against leakage at the edges. A photograph of the resulting modified PSD is shown in Figure 4.

Prototype reduced-rate PSD's were tested in the Battelle dosimeter test facility using procedures previously reported (*1*, *2*). Exposures to test atmospheres having nominal concentrations of each component in the range 1–10 ppbv were made in triplicate at each of four time periods ranging from 30 min to 24 h. The air velocity for these tests was maintained at 50 cm/s. Test compounds were chosen having a broad range of retention volumes in order to evaluate the performance of the modified PSD as a function of retention volume and exposure time. For these tests, exposure concentrations were not held constant but rather were allowed to decay smoothly at about 1.9% per hour as determined by the device sampling rates and the dilution rate of the exposure chamber.

Table I. Summary of Reduced Rate PSD Results

chemical	D^b	V_b^c	apparent sampling rate[a] 0.5 h	4 h	8 h	24 h	R_0	R/R_{calcd}[d]
acrylonitrile	6.35	4.9	2.34	8.79	3.55	1.46	3.06	1.15
			2.26	5.64	3.31	2.04		±28%
			2.45	7.38	3.27	1.70		n = 9
1,1-dichloroethylene	5.51	2	2.34	2.02	1.81	1.23	2.66	1.17
			2.12	1.65	1.62	1.13		±36%
			2.34	1.90	1.61	1.20		n = 1
dichloromethane	(6.31)[e]	5.5	1.54	2.65	2.02	1.53	3.04	0.89
			1.42	2.07	1.69	1.57		±19%
			1.77	1.90	1.71	1.81		n = 9
chloroform	5.33	18.9	(ND)	2.28	2.20	1.73	2.57	0.95
			2.82	1.62	1.91	2.57		±20%
			3.25	2.18	1.86	2.41		n = 11
2,2-dichloroethane	5.44	24	2.68	2.84	3.20	2.70	2.62	1.10
			2.18	1.94	2.79	2.47		±4.7%
			2.73	2.74	2.85	2.48		n = 9
1,1,1-trichloroethane	4.76	11.8	2.11	2.09	2.34	2.39	2.29	1.06
			2.53	1.50	2.06	2.29		±19%
			2.14	2.17	2.08	2.31		n = 12
benzene	5.59	42.5	2.82	2.76	2.79	2.35	2.69	0.96
			4.19	2.12	2.49	2.27		±8.6%
			4.79	2.57	2.43	2.18		n = 10
trichloroethylene	5.25	39.3	2.53	2.57	2.54	2.67	2.53	0.98
			2.37	1.90	2.11	2.42		±11%
			3.40	2.42	2.21	2.56		n = 11
trans-1,3-dichloropropene	4.76	335	2.00	2.74	2.63	2.57	2.29	1.19
			2.46	1.80	2.50	2.93		±8.2%
			3.15	2.58	2.65	2.90		n = 10
toluene	5.09	193	2.34	2.57	2.56	2.33	2.45	1.00
			3.12	1.79	2.27	2.50		±5.2%
			3.90	2.28	2.39	2.53		n = 9
tetrachloroethylene	4.57	154	1.32	2.35	2.26	2.53	2.40	0.91
			1.78	1.63	2.10	2.24		±13%
			2.18	2.17	2.14	2.50		n = 11

[a] Results for three PSDs listed in sequence. [b] Diffusion coefficient, cm²/min. Lugg, G. A. *Anal. Chem.* **1968**, *40*, 1072–1077. [c] Retention volume, L/g. Krost, K. J.; Pellizari, E. D.; Walburn, S. G.; Hubbard, S. A. *Anal. Chem.* **1982**, *54*, 810–817. [d] Mean, relative standard deviation, and number of included points for ratio of observed rate to rate calculated with eq 1. [e] Diffusion coefficient estimated by method of Fuller et al. Fuller, E. N.; Schettler, P. D.; Giddings, J. C. *Ind. Eng. Chem. Fundam.* **1968**, *58*, 19–27.

RESULTS AND DISCUSSION

Results of the laboratory evaluation of the reduced-rate PSD are shown in Table I. For the most part, the measured sampling rates for the reduced rate PSD agree well with

calculated rates, and the relative standard deviations are consistent with deviations previously noted in this laboratory for the standard PSD (*1*) and other passive dosimeters (*3*). A statistical analysis of the entire data set suggests that differences between individual devices may contribute about 6% to the total relative standard deviation. Standard deviations are largest for those chemicals having low retention volumes, as anticipated from consideration of Figure 3. It will be noted from the data in Table I that some points were rejected in the mean and standard deviation calculations. These rejections were made for points more than two standard deviations from the mean.

With nominal sampling rates of 2.5 cm^3/min, the curves shown in Figure 3 suggest that these reduced-rate PSD's should be usable for 24-h sampling of chemicals having retention volumes as low as 15 L/g and for 8-h sampling of chemicals having retention volumes as low as 5 L/g. This is a marked improvement over the unmodified PSD (nominal sampling rate = 80 cm^3/min), which was limited to 2–4-h sampling for many VOC's of interest to the air monitoring community.

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Registry No. Acrylonitrile, 107-13-1; 1,1-dichloroethylene, 75-35-4; dichloromethane, 75-09-2; chloroform, 67-66-3; 1,2-dichloroethane, 107-06-2; 1,1,1-trichloroethane, 71-55-6; benzene, 71-43-2; trichloroethylene, 79-01-6; *trans*-1,3-dichloropropene, 10061-02-6; toluene, 108-88-3; tetrachloroethylene, 127-18-4.

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